Physica C 214 (1993) 297–306
North-Holland

PHYSICA C

Formation and characterization of $YBa_2Cu_3O_{7-\delta}$ high-T_c thin films by MOCVD with single mixed precursor

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Received 5 March 1993
Revised manuscript received 8 June 1993

In view of the promising role of the MOCVD technique in the advance of YBCO high-T_c superconducting thin films grown for device applications, a simplified chemical vapor deposition system with a single mixed organometallic precursor was built and tested. Single phase $YBa_2Cu_3O_{7-\delta}$ films with T_c values around 90 K were readily obtained on (100) YSZ and (100) MgO substrates with a normal precursor mass transport. Investigations indicate that, in addition to the gas phase stoichiometry as a major factor, the phase composition and crystallite orientations of the YBCO films were considerably affected by the oxidation agent (partial pressure and concentration) as well as the substrate temperature. The films could be either highly oriented (00*l*) or (100) and/or (110) orientation dominated. A single phase $Y_2Cu_2O_5$ film with (002) orientation was obtained from a Ba deficient gas phase. The variation in superconducting behavior of the YBCO thin films deposited under different conditions was not only related to these phases but also to the growth orientation. The film uniformity and flatness are examined and discussed in terms of the gas flow pattern in the reactor.

1. Introduction

Soon after the discovery of high-T_c superconducting (HTSC) oxides, MOCVD was proposed for preparing high-T_c superconducting thin films [1]. It is now capable of producing high-T_c superconducting (HTSC) thin films comparable in quality to those prepared by any other methods, such as electron beam evaporation, sputtering, laser ablation and molecular beam epitaxy [2]. As generally accepted [3], the MOCVD technique has demonstrated its superior advantages in making large area high quality HTSC thin films and will play a major role in the advance of device applications of HTSC thin films over the next few years.

The organometallic compounds used in MOCVD preparation of HTSC oxide thin films are most frequently metal beta-diketonates. High-T_c superconductors as multi-component oxides demand a multi-source CVD system for thin film deposition. Because the volatility and stability of the organometallic precursors are strongly dependent on temperature, system pressure and carrier gas flow rate, it has been difficult to control the gas phase composition, and hence film stoichiometry. Since this is the prerequisite for producing large area uniform growth, a great deal of effort has been expended in order to overcome these problems. In addition to addressing the precursor mass transport process for controlling the composition [4,5], a number of modifications and new alternative techniques have been developed. Hiskes et al. [6], developed a single source MOCVD technique in which a mixture of organometallic compounds in the appropriate stoichiometric ratio, is fed collectively into a heater, and vaporized. The vaporized organometallics are then carried to the heated substrate. This technique appears to be, in principle, capable of avoiding the harmful effects produced by fluctuations in operating conditions, such as temperature, system pressure and carrier gas flow rate [7].

In this work a simple MOCVD apparatus following the ideas about mixed solid precursors by Hiskes et al. [6] was built and tested. The emphasis is put

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on YBCO film formation and its relation to operation conditions.

2. Experimental

2.1. Apparatus and operation procedure

The MOCVD apparatus used in this work is schematically shown in fig. 1. It consists of a precursor vaporizer made of pyrex glass and a quartz reactor 60 mm in diameter. A quartz hot finger with a stainless steel heat sink (25 mm in diameter) on its bottom as the substrate holder is placed in the reactor. The substrate holder is heated by a halogen lamp inside of the quartz tube. The precursors for the YBCO films are diketonate of tris(2,2,6,6,-tetramethyl-3,5-heptanedionato)yttrium ($Y(thd)_3$), bis(2,2,6,6-tetramethyl-3,5-heptanedionato)barium ($Ba(thd)_2.OH.2H_2O$) and bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper ($Cu(thd)_2$). A mixture of powders of $Y(thd)_3$, $Ba(thd)_2.OH.2H_2O$ and $Cu(thd)_3$, in the ratio of, or close to, Y:Ba:Cu = 1:2:3, is made compact in a glass tube. In these chemical formulae thd means *t*etramethyl-*h*eptane-*d*ionato, where the italic letters are the source of the acronym thd. This radical is also known as dpm or dipivoloylmethane. The tube has a 2 mm wide venting slit. During CVD operation, the charged tube which is loaded in the vaporizer is slowly advanced with a Unislide motor driven screw assembly into the heating zone serviced by an infrared lamp. Upon exposure to the infrared source, the mixed organometallics are vaporized, and the precursor vapors are swept away by argon carrier gas at a pressure of 5–7 Torr. After being mixed with oxygen from another gas inlet, the mixed vapor precursor is transported into the quartz reactor through the connecting tubing, which is heated to 250–300°C in order to avoid condensation of any organometallic vapors.

The substrates used in this work are YSZ (100), YSZ (110) and MgO (100) single crystal wafers. As seen from fig. 1, the substrate holder is heated by a tungsten halogen lamp and the substrate temperature is measured by a thermocouple in the stainless steel plate of the holder. The temperature can rise up to 850°C within 5 min. When the gas stream is switched from by-pass into the reactor, the YBCO film starts to grow. After growing for 50–100 min the precursor feeding and carrier gas (Ar) are stopped and the substrate temperature is raised to a higher temperature, usually around 850°C in flow oxygen at an ambient pressure of 740–760 Torr for 15 min. After that, the temperature is decreased to 450–500°C and held for 80–100 min until the tetragonal to orthorhombic transition of the deposited film is completed; then the power is turned off to cool the system down to room temperature. Typical opera-

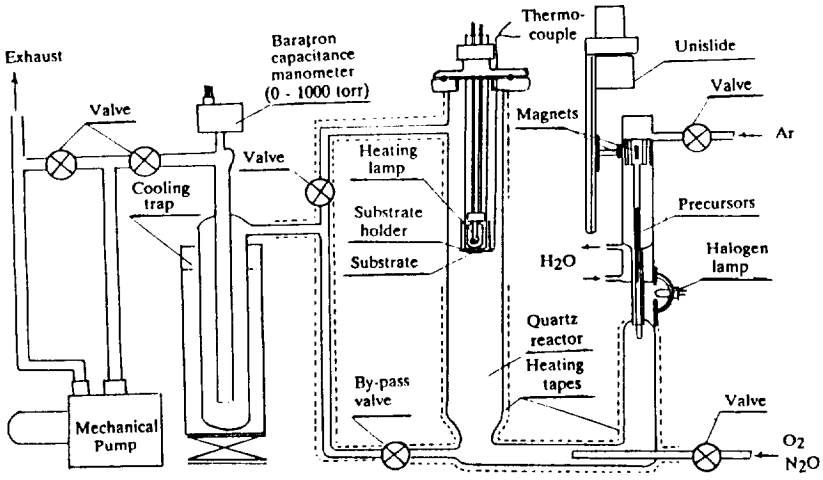

Fig. 1. Schematic diagram of the MOCVD system with single mixed precursor.

Table 1
Typical operating parameters of the MOCVD system

Substrate	YSZ (100), YSZ (110) and MgO (100) 25 mm, 13 mm or 10 mm in diameter
Precursor feed velocity	0.3–1.0 mm/min
Voltage of source lamp	55–70 volts
Carrier gas (Ar) flow rate	150–300 sccm (standard cc/min)
Oxygen flow rate during growth	200–300 sccm
Oxygen flow rate in post-annealing	50–100 sccm
Substrate temperature	750–830°C for film deposition 830–850°C for in situ post-annealing 450–500°C for phase transition process
Temperature of precursor transport line	250–300°C
Growth time	50–100 min
Post-annealing time	15 min
Phase transition process	60–100 min

tion parameters are summarized in table 1.

2.2. Characterization of YBCO thin films

XRD patterns of the YBCO films are taken on a Nicolet X-ray diffractometer (Siemens), using Cu Kα radiation, 50 kV and 30 mA, for identification of phase and growth orientation. A S-570 scanning electron microscope (Hitachi, Japan) has been employed to observe the microstructure of the films. Photographs are taken for both the surface morphology and section profiles. In order to increase the contrast of different phase grains, both backscattering electron image mode and inverted contrast mode were utilized. The surface morphology of some samples was also displayed in three dimensions by an atomic force microscope (AFM). The composition of the films and the distribution of Y, Ba, and Cu along the film surface are examined by using energy dispersion analysis of X-rays (EDAX). A bulk pure phase $YBa_2Cu_3O_{7-x}$ specimen was used as a standard.

The resistance–temperature measurements of the samples were done using a normal four probe technique. A Linear Research LR-400 (low frequency) four wire AC resistance bridge with a measurement resolution of 10 μΩ was used for resistance measurements.

In order to determine the thickness and surface flatness of the films, a Sloan Dektak surface measurement system with a fast leveling module was employed. The measurement determination resolution was about 2 nm. For film thickness determination, the film is chemically etched to make a stripe groove. The scanning head, a diamond stylus, of the profilometer is scanned on the specimen surface across the groove. For some selected samples, a three-dimensional display of the film surface was obtained by using a phase measurement interference microscope that provided nanometer height resolution over a 630 μm×617 μm rectangle and a 2.51 mm×2.45 mm rectangle.

3. Results and discussion

As seen from the sketch of the apparatus shown in fig. 1, it can be operated simply and efficiently because of the specially designed precursor vaporizer with only two gas inlets. Indeed, after the substrate and precursor cartridge tube are loaded in the system and the temperature of the precursor transport lines raised to the range of 250–300°C (accurate temperature control is not necessary), the precursor mass transport can be performed immediately by turning on the heating lamp. Moreover, the temperature of the substrate can reach a desired value (750–800°C) within 3–5 min. The by-pass in the system enables the film growth to start in a gas phase stream whose composition is exactly the same as the mixed solid source.

We have observed that mass transport of the precursor is less sensitive to the operation parameters such as heater power for precursor vaporization and

carrier gas flow rate, just as predicted theoretically [7]. However, it was found that if the precursor was handled in (grinding and packing) or exposed to ambient air, even for as short a time as one hour, its vaporization and mass transport turned out to be rather poor. A yellow liquid was formed and afterwards it became black and remained on the wall of the cartridge glass tube. The black substance was identified by EDAX to be mainly a barium containing substance, indicating that the barium beta-diketonate was responsible for the yellow liquid formation due to its absorption of moisture. A reduction of the barium concentration in the gas phase would, of course, result in a lack of sufficient barium content in the deposited film. Figure 2(a) is the XRD pattern of an earlier film (sample YBCO-007), which was deposited with poor precursor transport. We can see, in addition to the very strong diffraction peak for YSZ (200) at $2\theta = 35.3°$, that there are two phases, an (001) oriented $YBa_2Cu_3O_{7-x}$ phase (123 phase) and a Y_2BaCuO_5 phase (211 phase) with a dominant (131) orientation. Referring to the phase diagram of the CuO–$YO_{3/2}$–BaO system shown in

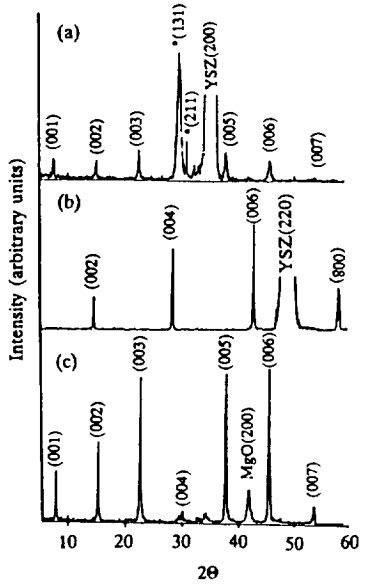

Fig. 2. XRD patterns of YBCO thin films obtained under various conditions; (a) a film of a two phase mixture of (131) oriented Y_2BaCuO_5 and (001) oriented $YBa_2Cu_3O_{7-\delta}$ deposited on YSZ (100) with Ba deficiency in precursor transport, (b) a perfect (002) oriented $Y_2Cu_2O_5$ thin film, (c) (001) oriented 123 phase film (YBCO-025), deposited with improved precursor mass transport.

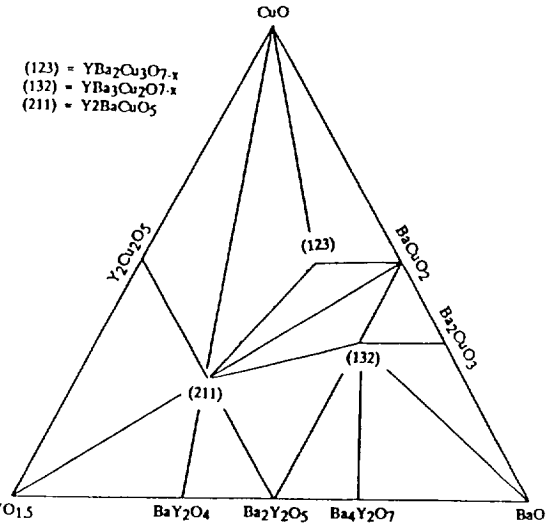

Fig. 3. Isothermal phase diagram of the $YO_{3/2}$–BaO–CuO system.

fig. 3, CuO and the 211 phase as well as the 123 phase would be formed when Ba is deficient in the system. However, no obvious CuO XRD peaks were observed, possibly because the deposited Cu_2O (thermodynamically stable above 650°C) sublimed or its nucleation was unfavored compared with other compounds during the deposition process. Figure 2(b) shows an XRD pattern, unfamiliar, but surely belonging to a single phase film which is highly oriented with a lattice spacing of 6.24 Å. This film was deposited on YSZ (110) at 830°C. During CVD operation a lot of the black substance was formed on the glass tube, indicating that the gas stream had developed Ba deficiency. EDAX measurements proved that there was a negligibly small Ba content (Cu:Ba = 75:1.5 in moles) in the film. Knowing that $Y_2Cu_2O_5$ has a crystal structure which belongs to space group Pna2 with $a = 10.799(2)$ Å, $b = 3.4990(5)$ Å, $c = 12.459(2)$ Å and $Z = 4$ [8], the peaks in fig. 2(b) can be identified as the (002), (004), (006) and (008) reflections of this material. Its insulating property and the stability in re-heating also confirmed that this film was pure $Y_2Cu_2O_5$. The reason why the film deposited in such a non-stoichiometric gas phase could be that a pure $Y_2Cu_2O_5$ phase with perfect (002) orientation may be attributed to the good lattice match between the a–b plane of $Y_2Cu_2O_5$ and the YSZ (110) face (the atomic distances are 5.09 Å and 3.599 Å) which would favor

preferential nucleation.

Precursor vaporization and mass transport can be improved by adjusting the carrier gas flow rate and the precursor feed rate. A larger flow rate and lower feeding velocity favors precursor vaporization. For a poor precursor source (e.g. one which was already exposed in air for some time) the preparation of a mixed precursor with more barium content would be a solution. For instance, an argon gas flow rate of 300 sccm (standard cc/min) and 0.3 mm of feeding velocity, using a precursor of Y:Ba:C: = 1:2.2:3 resulted in an almost pure 123 phase film with perfect (001) orientation on the MgO (200) substrate (fig. 2(c)). The $R-T$ curve of this sample showed metallic behavior as the temperature was decreased and a superconducting transition above 90 K with a zero resistance temperature higher than 85 K. Experiments demonstrated that if the mixed precursor was newly prepared in a dry glove box filled with ultra dry nitrogen or helium, the precursor could be transported completely by argon gas with an even lower flow rate (< 150 sccm). This confirms the importance of precursor purity, particularly the necessity of avoiding water absorption. The YBCO films prepared lately under better conditions usually exhibit a perfect (001) orientation and a zero resistance temperature of around 90 K.

Other operation parameters, such as the substrate temperature and the oxygen concentration and partial pressure in the gas phase, also considerably affect the formation of the $YBa_2Cu_3O_{7-\delta}$ phase. It was found that when the oxygen partial pressure in the mixed gas stream was below 40 %, the films deposited at a typical substrate temperature (750–850°C) were usually very thin, grey in color and exhibited a high resistance. In contrast, the YBCO films which were essentially a pure $YBa_2Cu_3O_{7-\delta}$ phase and which showed a better superconducting transition were always obtained from experimental runs with higher oxygen partial pressure (> 50%). But if the oxygen concentration in the gas stream was lower (e.g. both Ar and O_2 were 200 sccm) one still could not guarantee that a single HTSC phase would be deposited. However, when N_2O was used as an oxidation agent, a single $YBa_2Cu_3O_{7-\delta}$ phase with perfect (001) orientation could be deposited under a N_2O partial pressure of less than 40%. This result is consistent with the report by Tsuruoka et al. [9]. It implies that only the active oxygen species, instead of all the oxygen molecules, determines the formation of the superconducting phase.

The XRD of the YBCO films deposited under the typical conditions mentioned in the last section illustrate that they were mostly c-axis preferentially oriented as in fig. 2(c). But sometimes, as shown in fig. 4, a-axis oriented films were also obtained. It was reported [10] that a-axis oriented films were often grown on (110) perovskite substrates (such as $SrTiO_3$) or grown on $SrTiO_3$ (100) at lower temperatures. In our case, an (100) oriented film with only a small amount of (001) oriented grains (fig. 4(a)) was formed on a MgO (100) substrate at a rather high temperature (840°C). Figure 4(b) is the XRD pattern of a better stoichiometric sample (YBCO-013). As can be seen, all the peaks are identified as belonging to the $YBa_2Cu_3O_{7-\delta}$ phase. But there are three differently oriented diffraction peaks: (110), (100) and (001), of which the first two are dominant. EDAX results on this sample indicated that the atomic percentages of Y, Ba and Cu were 21.2, 16.5 and 62.3, respectively. That is,the Y and Cu contents are in the right ratio (1:3), while the Ba content deviates a lot from the proper stoichiometry, which agrees with the observation of the precursor

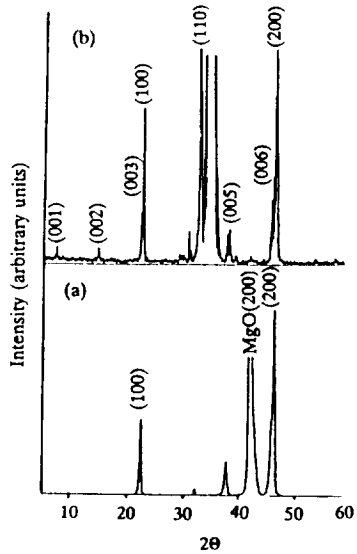

Fig. 4. XRD patterns for some single phase $YBa_2Cu_3O_{7-\delta}$ films with crystallite orientations other than (00/), (a) (100) orientation dominated film on MgO (100) (YBCO-022), (b) (100) and (110) orientations dominated film on YSZ (100) (YBCO-013).

vaporization. But it seems that the Ba percentage value, obtained from EDAX, is too low for this film. Because the EDAX based composition is located within a triangle whose apexes are CuO, Y_2BaCuO_5 and $YBa_2Cu_3O_{7-\delta}$ in the phase diagram of the CuO–$YO_{3/2}$–BaO system (fig. 3), if accurate, the XRD should have revealed the presence of the other two compounds as well as the 123 phase. However, the XRD (fig. 4) results indicate that the film is composed of a basically pure 123 phase with (110) and (100) orientations dominating. These inconsistencies possibly resulted from the different capabilities of the two techniques, including their different detection limits and detected areas and depths. EDAX essentially detects the local composition of the top layer. Thus the result from EDAX implies that there was an Y and Cu rich gas phase during the deposition of the final top layer of this film.

The two films whose XRD patterns are shown in fig. 4 look visually as smooth and shiny as a mirror. SAM photographs revealed that these films were dense polycrystalline layers with well defined grains in the order of 200–500 nm. The backscattering and inverted backscattering electron images exhibited different degrees of darkness which demonstrated that there are differently oriented grains. A three-dimensional color photo of the film YBCO-22 by AFM, shown in fig. 5, displays a vivid surface morphology with a peak to valley of less than 150 nm. In contrast, SAM morphology of the perfect (001) oriented thin films is quite different. Some bigger grains exist on the growing surface. Figure 6 shows oblique displays of randomly chosen rectangles 630 μm×617 μm of the film (6a) and substrate (6b) surfaces. The vertical display for the film extends over 20 nm, while for the substrate it is 10 nm. On this scale, the variation is about 10 nm. And, although the film has many peaks which can be attributed to the individual grains, its overall non-uniformity appears to be about a factor of two higher than that of the substrate. Figure 7(a) shows a profilogram measured with a Dektak surface profilometer scanned across a stripe chemically etched along the diameter of sample YBCO-22 (25 mm in diameter). It gives both

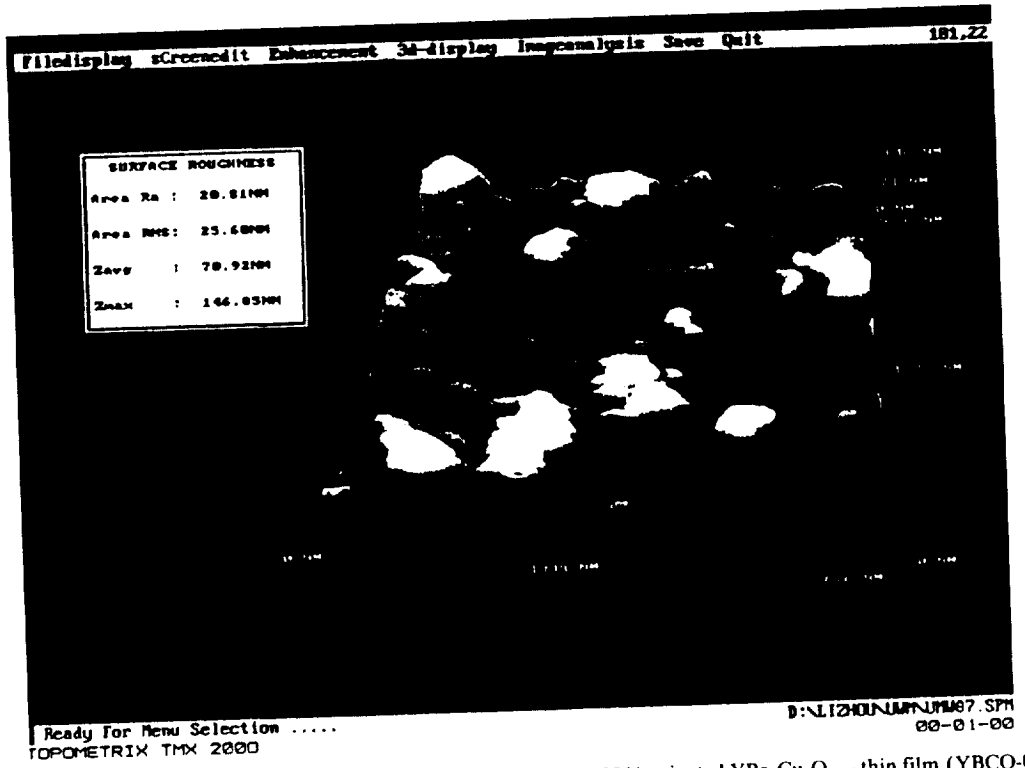

Fig. 5. A three-dimensional display of the surface morphology of a (001) oriented $YBa_2Cu_3O_{7-\delta}$ thin film (YBCO-022).

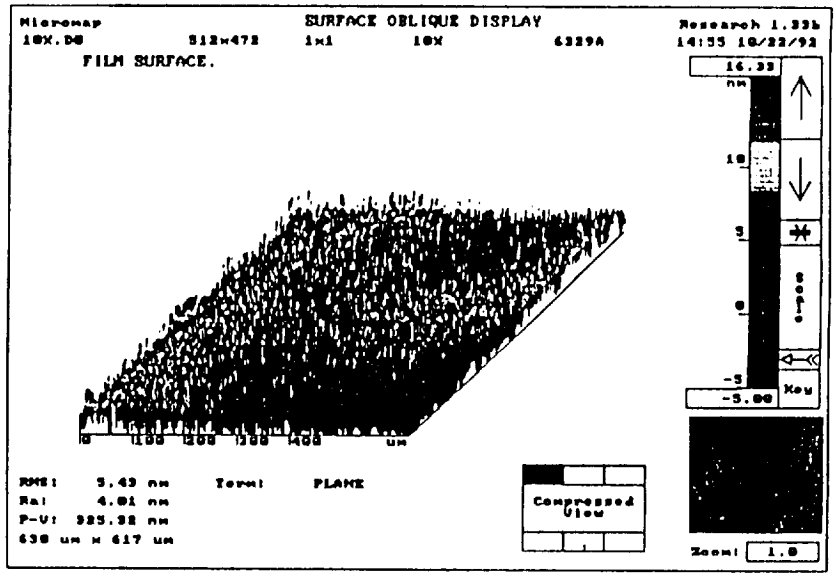

Fig. 6. Surface oblique display of the film YBCO-013 by optical interference microscopy.

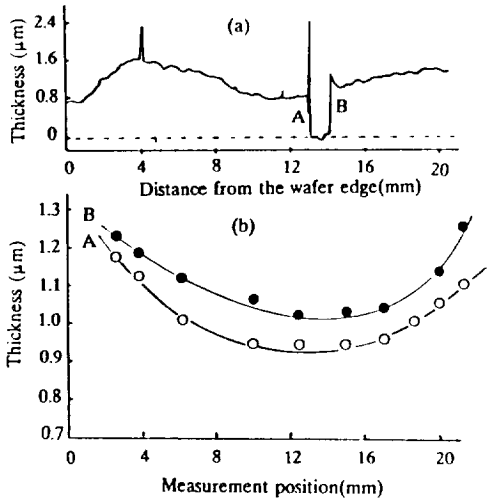

Fig. 7. Thickness uniformity of a film deposited on MgO (100) (YBCO-22), (a) a profilogram across a chemically etched stripe on the film surface, (b) the thickness distribution along the stripe edges.

the film thickness and the surface smoothness. We may see that, except for individual grains which cause sharp peaks, the surface local roughness may be estimated to be below 50 nm.

Figure 7(b) illustrates thicknesses along the two edges of the stripe. It reveals that the film has a particular thickness distribution: the central part is about 200–250 nm thinner than the outer part. In fact, fig. 7(a) taken at 90° to the stripe edges, also shows this effect. We know that at the substrate temperatures higher than 600°C the deposition rate of $YBa_2Cu_3O_{7-\delta}$ becomes independent of the substrate temperature. In this region, the deposition rates are limited by the mass transport of the reactive species

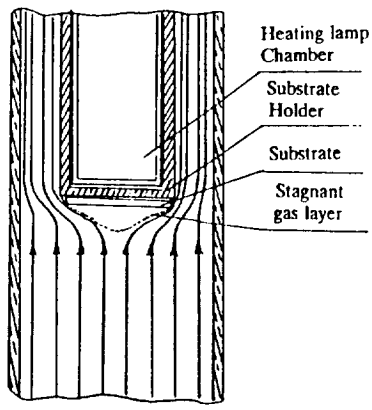

Fig. 8. A gas flow pattern model in the reactor near the substrate, showing the existence of a stagnant flow layer in the central part.

towards the substrate surface [11] . The fluid hydrodynamics and geometry of the system will affect the mass transport. The results obtained in fig. 7 could be attributed to a specific gas stream flow pattern near the growing surface. As schematically shown in fig. 8, near the central part of the wafer there is a stagnant boundary layer in which the gas flow velocity is much lower than near the outer part. Thus, there is an insufficient mass transfer via diffusion across the stagnant boundary layer, while the outer part has an efficient mass transfer process due to the fast gas flow which produces a thinner boundary layer. This indicates that even in such a low pressure CVD system, fluid hydrodynamics should still be taken into account in order to obtain a smooth surface and uniform thickness. It is possible that surface smoothness and uniformity in thickness may be improved by enlarging the reactor diameter and by inserting a diffusion barrier in the reactor chamber. A new reactor is being designed which will incorporate these modifications. If the substrate surface is uniform and the temperature and vapor pressure are uniform on the substrate surface, large area and high quality films can be obtained. Hiskes et al. [12] have successfully deposited 100 mm diameter YBCO (001) films on uniform substrates.

It has been demonstrated that the superconducting characteristics of the YBCO thin films obtained under different conditions vary, depending on both the type of YBCO phases and the crystallographic orientations that are deposited. The R–T curves of the YBCO films with perfect (001) orientation show a metallic behavior in the normal state and reach zero resistance at a temperature higher than 85 K as seen in fig. 9. Figures 9(b) and (c) are the R–T curves for the films whose XRD patters are shown fig. 4. They are single phase $YBa_2Cu_3O_{7-\delta}$ films, but with dominant crystallite orientations other than (001). It can be seen that they first exhibit a semiconducting behavior as the temperature decreases and then a superconducting transition which is below 90 K. Some samples even exhibit a plateau around 60 K (fig. 9(c)), demonstrating a lower temperature superconducting phase due to low oxygenation. The low critical temperatures T_c imply that the boundaries between (100) and/or (110) oriented grains have large electrical junctions resistivities, which would yield zero resistance at lower temperatures for a percolative network [13]. Figure 10 shows both an XRD pattern and an R–T curve for a sample (YBCO-046) which was deposited at a lower temperature (770°C) without in situ high temperature annealing. This film

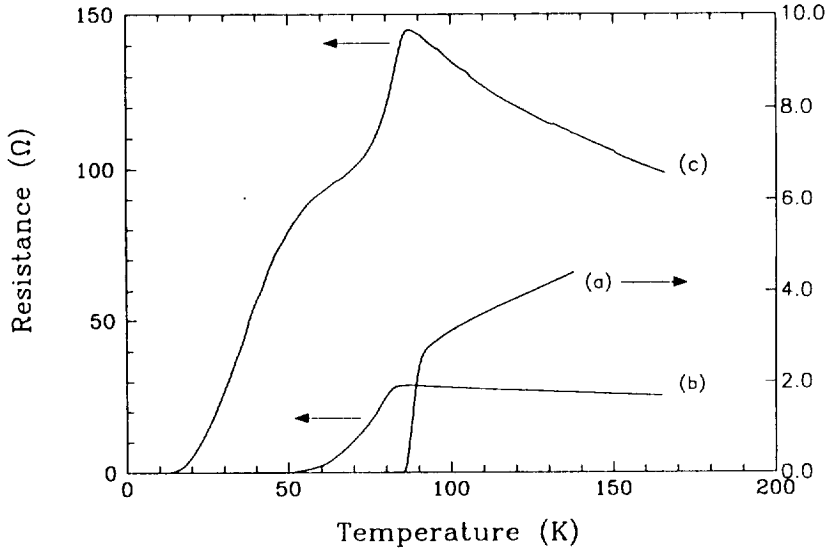

Fig. 9. R–T curves of the films whose XRD patterns are shown in fig. 4, (a) sample YBCO-13, (b) sample YBCO-022, (c) sample YBCO-025.

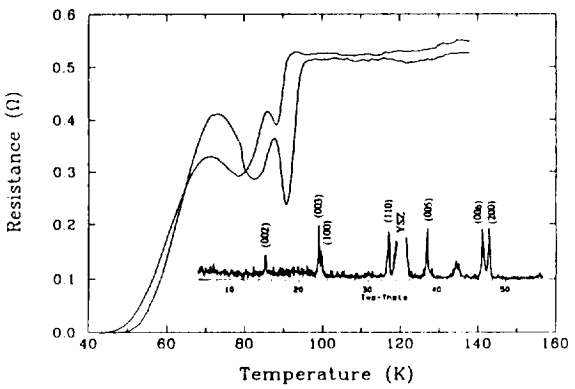

Fig. 10. XRD and R–T curve for a 123 phase sample with multi-orientations, showing the unique multi superconducting transitions.

is composed of (001), (110) and (100) oriented grains, comparable to each other in fractional quantities, according to the relative intensity of their XRD peaks. Here, we see an even more complicated R–T curve, which seems to indicate two lower temperature superconducting phases as well as the normal 90 K superconducting phase. It might be interesting to correlate this electric behavior with the specific microstructure of the film. However, for the practical purpose of device applications purely oriented growth, either a-axis or c-axis and even epitaxial single crystal growth are preferred, and polycrystalline multi-oriented growth should be avoided. Though much more work is needed, one thing is certain: the deposition mechanism on the growing surface, including surface reactions, nucleation, grain growth and their relation to deposition parameters, should be considered.

4. Conclusions and remarks

A simplified MOCVD system using mixed single organometallic precursors demonstrated good performance. $YBa_2Cu_3O_{7-\delta}$ thin films on large area YSZ (100) and MgO (100) substrates (25 mm in diameter) were readily obtained. The deposition rate was about 100 nm/min. It was found that the key point to obtain good composition control was to keep the organometallic precursor absolutely dry. If the precursor was exposed to air for a long time, the mixed precursor easily liquified due to moisture adsorption by the Ba β-diketonate and resulted in Ba deficient gas phase which would give a multi-phase film. In some extreme cases when the Ba mass transport was too poor, even a highly (002) oriented pure $Y_2Cu_2O_5$ film was obtained. In addition, a higher oxygen partial pressure of the gas phase ($P^{(O_2)} > 40\%$) was necessary for the formation of the superconducting YBCO thin films. Moreover, the use of N_2O as a substitute for oxygen as the oxidation agent could decrease this figure as well as lower the deposition temperature. These facts are certainly related to the deposition mechanism.

XRD indicated that the films could be either highly (001) oriented or (110) and (100) orientation dominated, depending mainly on the film composition and the deposition conditions. The temperature dependence of the resistance of the films obtained so far exhibited either semiconducting behavior or metallic behavior above the superconducting transition temperature. It was demonstrated that the semiconducting behavior, the tail phenomenon on the R–T curves, and the existence of lower temperature superconducting phases are associated with the microstructure of multi-oriented grains in the films. The rather low transition temperature and large transition width of some of the early films could be attributed to a deficiency in barium, which was corrected by preparing and loading the mixed organometallic precursors in a dry glove box .

SAM and AFM revealed a quite characteristic surface morphology for the YBCO thin films with different orientations. The (001) oriented 123 phase films have granular grains formed on the surface, while (100) and/or (110) oriented layers consist of more dense and well defined grains in sizes of 200–500 nm. The local surface smoothness and flatness were determined by different techniques to be of the order of 50 nm. Particularly, it was found that the thickness uniformity was considerably affected by the gas flow pattern adjacent to the growth surface.

In order to avoid the formation of multi-oriented grains and to obtain uniform quality YBCO HTSC thin films, the surface deposition process, such as surface reaction, nucleation, grain growth and their relation to operation parameters as well as the fluid hydrodynamics of the system should be further investigated.

Acknowledgements

The authors would like to express their grateful thanks to R. Paddock, M. Gillott, M. Mclaurin, M. Mitchell and R. Ponton for their assistance in various measurements and constructions. This research work was supported by NASA under contract #NAG3-1274 and partially supported by the UWM Graduate School and the Laboratory for Surface Studies.

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